Featured Highlights

from the National Synchrotron Light Source

Revealing a Key Intermediate in Green Oxidation Catalysis

As industrial processes release pollutants such as dyes, pesticides and other harmful chemicals into the Earth's water, a team of researchers is turning to a class of "green" catalysts for cleanup. Developed at Carnegie Mellon University in 1995, Fe-TAMLs – short for iron tetra-amido macrocyclic ligand activators – destroy a multitude of pollutants in water by accelerating cleansing reactions with hydrogen peroxide. Since then, researchers have worked to determine exactly how these processes work, and recently, they figured out another piece of that puzzle. Through studies that included EXAFS investigations at the NSLS, researchers from CMU and the University of Minnesota have isolated and characterized a species thought to be a key intermediate in the Fe-TAML reaction with peroxides and oxygen.

Authors (top, from left) Deboshri Banerjee, Emile Bominaar, Arani Chanda, and Terry Collins, (bottom, from left) Sujit Mondal, Eckard Münck, Filipe Tiago de Oliveira, and Lawrence Que

The results of the study, published in the February 9, 2007, issue of *Science*, lend weight to the theory that Fe-TAML catalysts work by separating hydrogen peroxide into water and an oxygen atom that is bound to the iron of the Fe-TAML. The resulting Fe-TAML-oxo complex then destroys undesirable molecules, rendering them less toxic and often proceeding to mineralization or near-mineralization. The inventor of these extremely active catalysts, CMU's Terry Collins, describes Fe-TAML reactions as "fire in water," because the activated peroxide carries out chemistry on many (but not all) carbon-containing compounds where the products resemble those of combustion.

Because of this high reactivity, the catalyst's developers had to build ligand systems that allow for the formation of iron-oxo complexes from the Fe-TAML activators without being rapidly destroyed by the highly reactive intermediates they enable.

The stable form of the iron used in the Fe-TAML starting catalyst complex is Fe(III), the state of iron found naturally in rust. However, during the reaction between peroxides and an Fe-TAML activator, the iron's oxidation state has been shown to pass through an Fe(IV) species and then proceed onto an Fe(V) species. This Fe(V)-oxo complex is thought to be a key reactive intermediate in Fe-TAML oxidation catalysis.

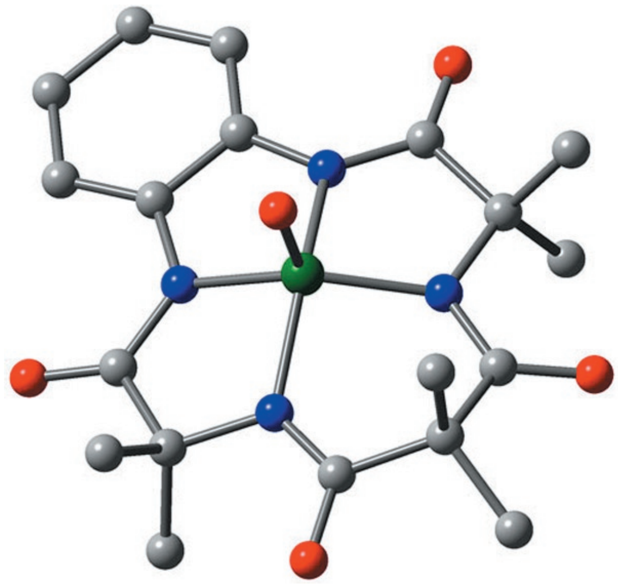
"For about the last 10 years, I've been convinced that the Fe(V)-oxo group existed," said Collins, the director of the Institute for Green Oxidation Chemistry at CMU's Mellon College of Science. "Proving it was another matter."

Atoms with high oxidation states, such as Fe(IV) and Fe(V), are difficult to trap because they're so reactive. In order to "catch" the Fe(V)-oxo group, the researchers set up a system in an organic solvent at a very low temperature (about –60 °C) because water's high freezing point prevented its use. They then titrated it in a very reactive peroxide.

Using x-ray absorption spectroscopy at NSLS beamline X3B, University of Minnesota researcher Lawrence Que's group combined with Collins' group and CMU's Mössbauer, EPR, and theory group (led by Eckard Münck) to reveal the long-sought chemical and electronic properties of the intermediate. This is the first characterization of an Fe(V)-oxo complex.

"This was a great challenge, and we've gotten to the top of this mountain," Que said. "Knowing these properties increases our ability to carry out the oxidation of compounds and helps us understand how iron agents might be working in environmental remediation."

That includes an increased knowledge about Collins' Fe-TAML catalysts, which have been demonstrated for a variety of uses including cleaning up water polluted at textile, pulp, and paper mills; removing sulfur from diesel fuel; destroying traces of endocrine-disrupting



The structure of the Fe(V)-oxo complex (green, iron; red, oxygen; blue, nitrogen; and gray, carbon.) For clarity, hydrogen atoms are not shown.

chemicals in water; killing anthrax spores and other water-borne infectious microbes; and even stopping dark-colored laundry from staining whites and lights in the wash.

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— Kendra Snyder